

# UNPUBLISHED PRELIMINARY DATA

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The George Washington University  
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## Organic Complexes of Transition Metals for Optical Maser Materials

During the period of April 1 to September 30, 1964, progress has been made in this work along four directions of attack: (1) synthesis and purification of materials, (2) spectroscopic measurements, (3) testing as optical masers and (4) theoretical work.

### 1. Synthesis of Materials

Several classes of transition metal complexes and chelates have been synthesized, as follows:

A. Rare Earth  $\beta$ -diketonates. The following  $\beta$ -diketones have been purchased (p) or synthesized (s):

Acetylacetone (p)	Di-m-nitrodibenzoylmethane (s)
Trifluoroacetylacetone (p)	p-Phenyldibenzoylmethane (s)
Hexafluoroacetylacetone (p)	Di-p-fluorodibenzoylmethane (s)
Dibenzoylmethane (p)	Benzoylacetone (p)
p-Methoxydibenzoylmethane (s)	Theonyltrifluoroacetylacetone (p)
Di-p-Methoxydibenzoylmethane (s)	Benzoyltrifluoroacetone (s)
m-Methoxydibenzoylmethane (s)	DiTheonymethane (s)
Di-m-methoxydibenzoylmethane (s)	Difuroylmethane (s)
p-Nitrodibenzoylmethane (s)	Diisonicotylmethane (s)
Di-p-nitrodibenzoylmethane (s)	Di-1-naphthoylmethane (s)
m-Nitrodibenzoylmethane (s)	Di-2-naphthoylmethane (s)

These ligands were purified by recrystallization, vacuum sublimation or distillation and identified by elementary analysis, melting points and molecular weight determination.

Chelates of Europium, Terbium and Gadolinium have been prepared from these liquids by titration with alcoholic ammonia or piperidine of a mixture of rare earth chloride (99.99%) and  $\beta$ -diketone in absolute ethanol to pH = 6.5

The chelates were purified by repeated recrystallization from appropriate solvents.

### B. $\alpha\alpha'$ -Dipyridyl Complexes.

$\alpha\alpha'$ -Dipyridyl complexes of trivalent rare earth ions have been prepared in absolute ethanol from Dipyridyl and anhydrous rare earth chloride (Eu, Tb, Pr, Gd, Sm and Yb)

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C.  $\beta$ -Ketomines.

Four  $\beta$ -ketomines were synthesized from dibenzoylmethane and benzoylacetone reacted with equimolecular amounts of aniline and p-nitroaniline. Europium chelates of these liquids were prepared analogous to the  $\beta$ -diketonates chelates.

D.  $\alpha,\alpha'$ -Diquinolyl Complexes.

Attempts have been made to prepare  $\alpha,\alpha'$ -Diquinolyl complexes of Eu, Tb, Gd, Sm and Yb. The identity of the materials has not been established.

E. Tris-cyclopentadienyl-Rare Earth Complexes.

Tris-methylcyclopentadienyl-samarium has been prepared and sublimed in high vacuum. Other rare earth analogous compounds are in preparation.

2. Spectroscopic Measurements

Absorption spectra of  $\alpha,\alpha'$ -dipyridyl,  $\alpha,\alpha'$ -diquinolyl, and  $\beta$ -ketoimine complexes have been determined in absolute ethanol in the UV-visible range with the Cary 14 Spectrophotometer.

Solvent and temperature effects on the fluorescence intensity of Europium  $\beta$ -diketonates have been evaluated in the boiling point-freezing point temperature range in 10 solvents with different dipole moments.

A lifetime apparatus has been set up, and improved flash lamps have been ordered.

3. A laser cavity for liquid laser testing is now available and the auxiliary equipment being prepared will make it operative in the near future, at NASA.

4. Theoretical work is in progress on the interpretation of the intramolecular energy transfer in  $\beta$ -diketonates based on fluorescence, phosphorescence, and absorption data. The effect of substituents in the different stages of the intramolecular energy migration, and symmetry, efficiency and transition probability problems are under consideration. Energy level calculation for rare earth tris-cyclopentadienyl complexes is also being pursued in parallel.

5. A manuscript entitled "Solvent and Temperature Effects on Fluorescence Emission of Europium  $\beta$ -Diketonates" has been submitted for publication to Spectrochimica Acta on the 5th of October 1964. [REDACTED]